

<b>LNDD</b>	<b>MODE OPÉRATOIRE</b>	Codification : M-AN -41 Version : B Date : 28/10/2005 1 / 2
<b>MODE OPERATOIRE D'ANALYSE POUR LA CONFIRMATION DE L'ORIGINE DES METABOLITES DE LA TESTOSTERONE PAR CPG/C/SMRI</b>		

### COLONNE

Type: DB17-MS JW Scien 122.4732  
 Longueur: 30m  
 Diamètre interne: 0.25mm  
 Epaisseur du film: 0.25µm

ASSURANCE QUALITÉ  
LNDD

### INJECTION

Mode: Splitless (insert splitless)  
 Température injecteur: 280°C  
 Volume injecté: 1µl-4µl  
 Solvants de rinçage ALS: Solvant A: Acétonitrile  
 Solvant B: Hexane

APPLICABLE le

28 OCT. 2005

### CONDITIONS GC

Température initiale: 70°C pendant 1 min  
 Gradient de température: 70->271°C à 30°C/min  
 271°C->281°C à 0.6°C/min  
 281°C pendant 3 min  
 281->300°C à 5°C/min  
 300°C pendant 5 min  
 45 min  
 Température finale: Ajuster le SI à environ 870s  
 Temps d'analyse:  
 Pression constante:

### INTERFACE

Piège à eau: -100°C  
 Ligne de transfert: 350°C  
 Four à combustion: 850°C

SPECIMEN

### CONDITIONS SM

Mode d'acquisition: ions 44, 45 et 46  
 Programmation de l'acquisition: Temps d'acquisition total: 2580s  
 à 100s RG open  
 à 130s RG close  
 à 160s RG open  
 à 190s RG close  
 à 220s RG open  
 à 250s RG close  
 à 750s HS close  
 à 2000s HS open  
 à 2400s RG open  
 à 2430s RG close  
 à 2460s RG open  
 à 2490s RG close  
 à 2510s RG open  
 à 2540s RG close

LNDD

## MODE OPÉRATOIRE

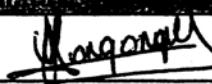
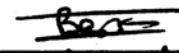
Codification : M-AN -41

Version : B

Date : 28/10/2005

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MODE OPERATOIRE D'ANALYSE POUR LA CONFIRMATION DE L'ORIGINE DES  
METABOLITES DE LA TESTOSTERONE PAR CPG/C/SMRI

ANNEE		DATE	REMARQUE
rédigé par	Cynthia MONGONGU	28/10/2005	
vérifié par	Caroline BASTIEN	28/10/2005	
vérifié par	Aurélie LAURENT	28/10/2005	
approuvé par	Jacques DE CEAURRIZ	28/10/2005	

N° Version	Motif	Date
1	Création du document.	27/05/2002
A	Acceptation du projet après conversion du tr du SI en seconde, création de la version A	14/10/2002
B	Révision biennale	28/10/2005

SPECIMEN

USADA 0330

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Batch Data Processing Results

Data File Name : 040806  
 Autorun Setup File Name : 040806  
 Blank Subtraction : Disabled  
 Background Subtraction : Disabled  
 Reference Gas : Enabled  
 Ref Gas Delta (C13) : -34.50  
 Ref Gas Delta (O18) : -19.30  
 Current Time : 22:17:03  
 Current Date : 04/08/06

Sample Details

Elemental Isotopic

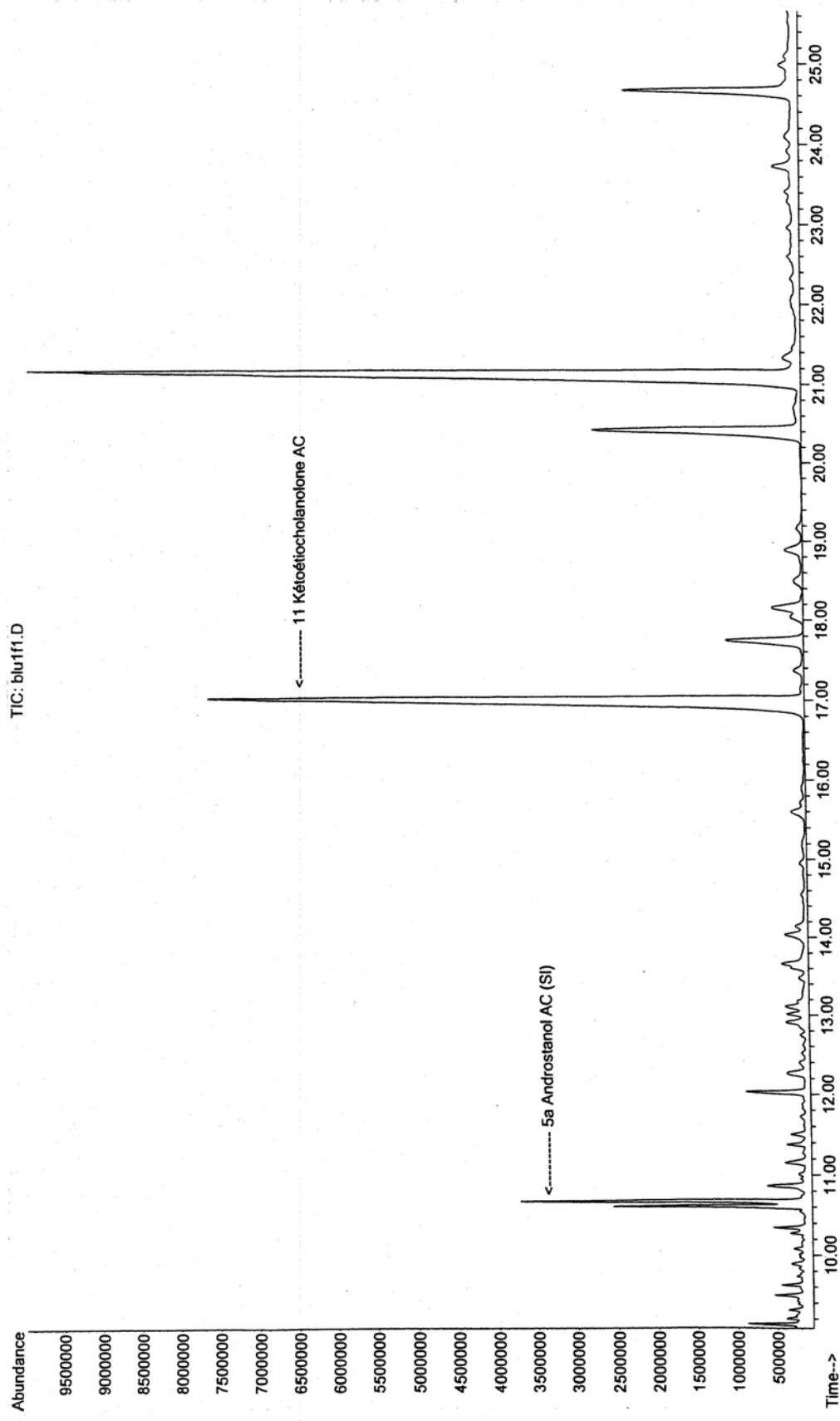
No.	Name	Weight (mg)	Ref Type	% Comp (C)	Delta (C13)	Delta (O18)
1	Stabilite 1	0.000	Sam			
2	Stabilite 2	0.000	Sam			
3	Stabilite 3	0.000	Sam			
4	Stabilite 4	0.000	Sam			
5	Stabilite 5	0.000	Sam			
6	Mix Cal IRMS 003-1	0.000	Sam		-31.30	-40.0
7	Mix Cal IRMS 003-2	0.000	Sam		-31.68	-40.0
8	Mix Cal IRMS 003-3	0.000	Sam		-31.42	-39.3
9	Mix Cal Acetate 001A-100ng inj	0.000	Sam			
10	Blu 1 Pool 4 F3/45uL inj 2uL	0.000	Sam		-31	
11	178/07 995474 F3/45uL inj 2uL	0.000	Sam		-3	
12	Blu 1 Pool 4 F1/120uL inj 2uL	0.000	Sam		-3	
13	178/07 995474 F1/150uL inj 2uL	0.000	Sam		-	
14	Blu 1 Pool 4 F2/1400uL inj 2uL	0.000	Sam		-	
15	178/07 995474 F2/850uL inj 2uL	0.000	Sam		-	
16	Mix Cal Acetate 001A-100ng inj	0.000	Sam		-	

Sample Details

No.	Name	Weight (mg)	Ref Type	Atom % (C13)	Atom % XS (C13)
-----	------	----------------	-------------	-----------------	--------------------

1	Stabilite 1	0.000	Sam		
2	Stabilite 2	0.000	Sam		
3	Stabilite 3	0.000	Sam		
4	Stabilite 4	0.000	Sam		
5	Stabilite 5	0.000	Sam		
6	Mix Cal IRMS 003-1	0.000	Sam	1.07683	-0.0344
7	Mix Cal IRMS 003-2	0.000	Sam	1.07641	-0.0348
8	Mix Cal IRMS 003-3	0.000	Sam	1.07670	-0.0345
9	Mix Cal Acetate 001A-100ng inj	0.000	Sam	1.08114	-
10	Blu 1 Pool 4 F3/45uL inj 2uL	0.000	Sam	1.07712	-0.
11	178/07 995474 F3/45uL inj 2uL	0.000	Sam	1.07560	-0
12	Blu 1 Pool 4 F1/120uL inj 2uL	0.000	Sam	1.07649	-0
13	178/07 995474 F1/150uL inj 2uL	0.000	Sam	1.07751	-
14	Blu 1 Pool 4 F2/1400uL inj 2uL	0.000	Sam	1.07826	-
15	178/07 995474 F2/850uL inj 2uL	0.000	Sam	1.07131	-
16	Mix Cal Acetate 001A-100ng inj	0.000	Sam	1.08271	-

File : D:\Msd22\Aout06\0408\b1u1f1.D  
Operator : 26 Aug 2006 14:26 using AcqMethod MAN\_52.M  
Acquired : 4  
Instrument : MSD22  
Sample Name: Blu 1 F1  
Misc Info : Blanc urinaire 1 Pool 4 Fraction 1 dans 100µL  
Vial Number: 4



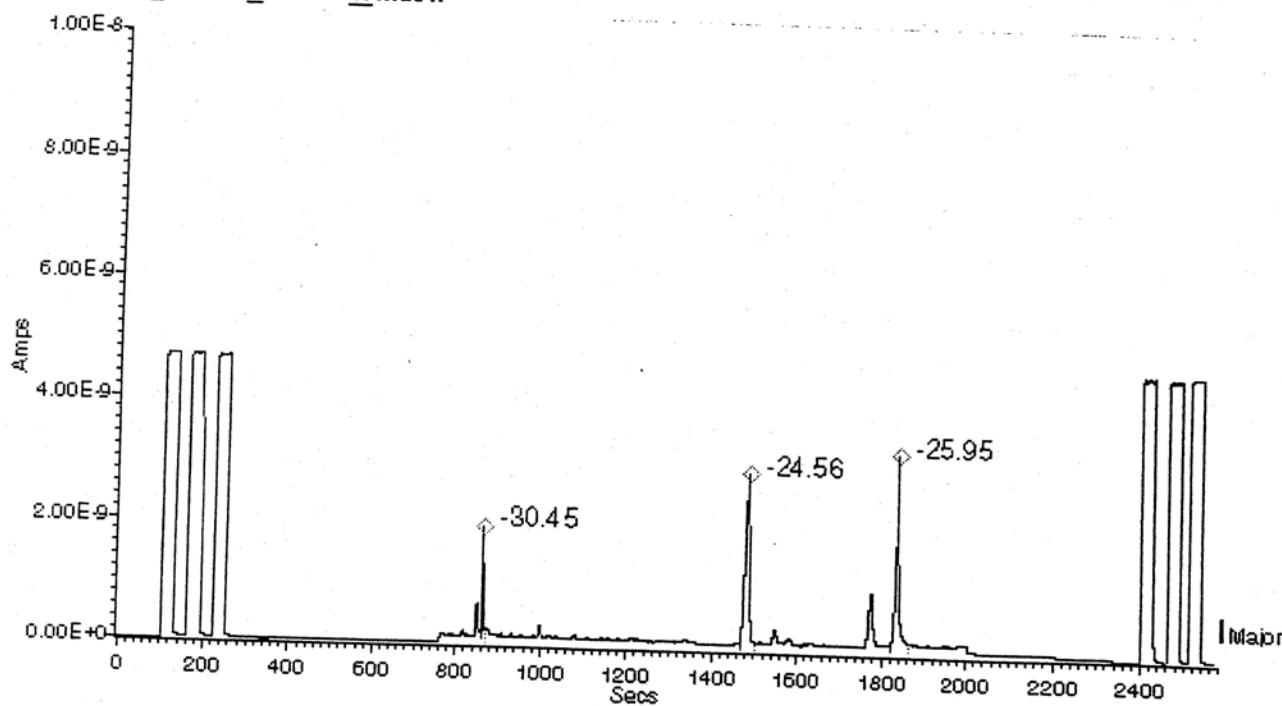
# DP Optima GC 1.67-2 - Manual DP

File Edit View Calculate Report Parameters Status Help

Data      Filename : DATA\_012      Folder : 040806  
Date : 04/08/06      Time : 18:33:24  
Comment : Blu 1 Pool 4 F1/120uL inj 2uL :  
Parameters      Automatic DP Params

## Data Processing Main Graph

Graph Cursor Lines Window



USADA 0333

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DOCUMENTATION PACKAGE.**

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### Data Processing Results

Data File Name : DATA\_012  
 Folder : 040806  
 Sample Name : Blu 1 Pool 4 F1/120uL inj 2uL  
 Sample ID :  
 Sample Position : 5  
 Injection Size : 0.0000  
 Sample Type : Sam  
 Method : M-AN-41  
 Batch Name :  
 RunTime User : micromass  
 Acquisition Time : 18:33:24 Date : 04/08/06  
 Current Time : 19:18:07 Date : 04/08/06

#### Analysis of Reference Gas Data

Ref Delta 13 = -34.50 Ref Delta 18 = -19.30

Time	Major	Ratio 2/1	Ratio 3/1
122.6	8.532E-8	1.1773E-2	4.2515E-3
182.6	8.541E-8	1.1773E-2	4.2517E-3
242.6	8.493E-8	1.1773E-2	4.2515E-3
2423.5	8.481E-8	1.1773E-2	4.2516E-3
2483.5	8.479E-8	1.1773E-2	4.2516E-3
2533.5	8.517E-8	1.1773E-2	4.2520E-3

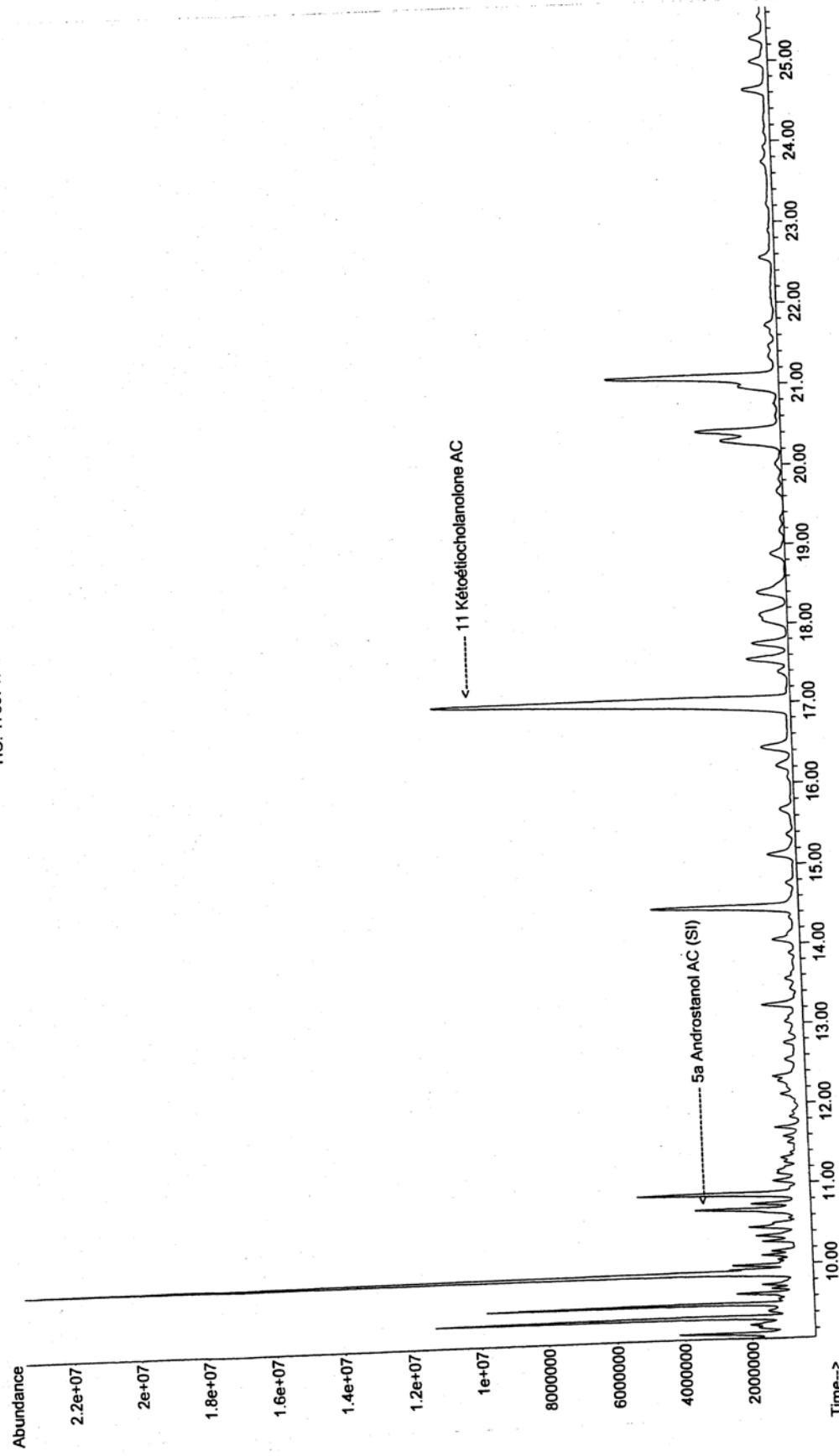
Std Dev Of Fit 1.3906E-7 1.7907E-7

#### Analysis of Sample Peaks, with Background Subtraction

CO2		Time	Height	Area	2/1	3/1	dC13Pk	dC13Bkd	dO18Pk	dO18
869.6	1.97E-9	9.0004E-9	1.1813E-2	4.1841E-3	-30.45	-64.35	-34.89	18		
1489.8	2.93E-9	3.0458E-8	1.1879E-2	4.1636E-3	-24.56	-62.12	-39.64	20		
1843.5	3.29E-9	3.8707E-8	1.1864E-2	4.1725E-3	-25.95	-58.90	-37.61	18		

File : D:\Msd22\Aout06\0408\17807474f1.D  
 Operator : 26 Aug 2006 14:59 using AcqMethod MAN\_52.M  
 Acquired : 4 Aug 2006 14:59 using AcqMethod MAN\_52.M  
 Instrument : MSD22  
 Sample Name: 178/07 B995474 F1  
 Misc Info : 178/07 B 995474 Fraction 1 dans 100µL  
 Vial Number: 5

TIC: 17807474f1.D



USADA 0336

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# Optima GC 1.67-2 - Manual DP

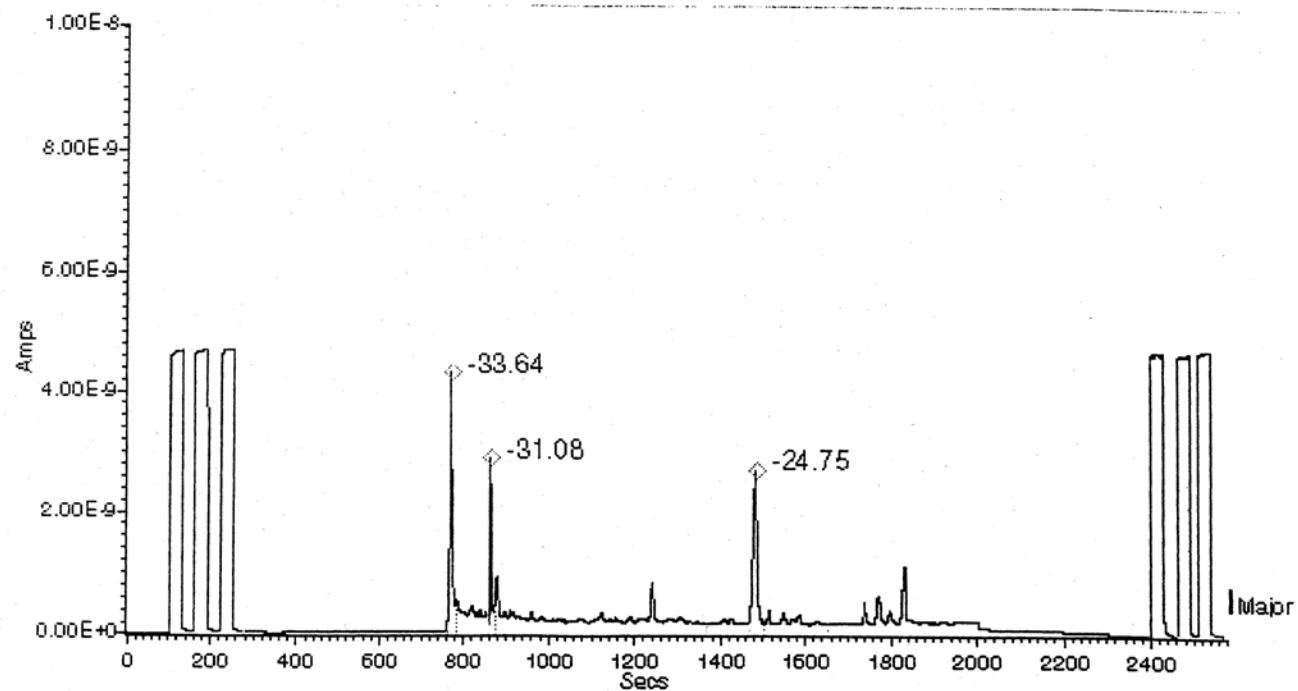
File Edit View Calculate Report Parameters Status Help

Data                   Filename : DATA\_013                   Folder : 040806  
                         Date : 04/08/06                   Time : 19:18:09  
                         Comment : 178/07 995474 F1/150uL inj 2uL

Parameters           Automatic DP Params

## Data Processing Main Graph

Graph Cursor Lines Window



USADA 0337

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### Data Processing Results

Data File Name : DATA\_013  
 Folder : 040806  
 Sample Name : 178/07 995474 F1/150uL inj 2uL  
 Sample ID :  
 Sample Position : 6  
 Injection Size : 0.0000  
 Sample Type : Sam  
 Method : M-AN-41  
 Batch Name :  
 RunTime User : micromass  
 Acquisition Time : 19:18:09 Date : 04/08/06  
 Current Time : 08:07:48 Date : 05/08/06

#### Analysis of Reference Gas Data

Ref Delta 13 = -34.50 Ref Delta 18 = -19.30

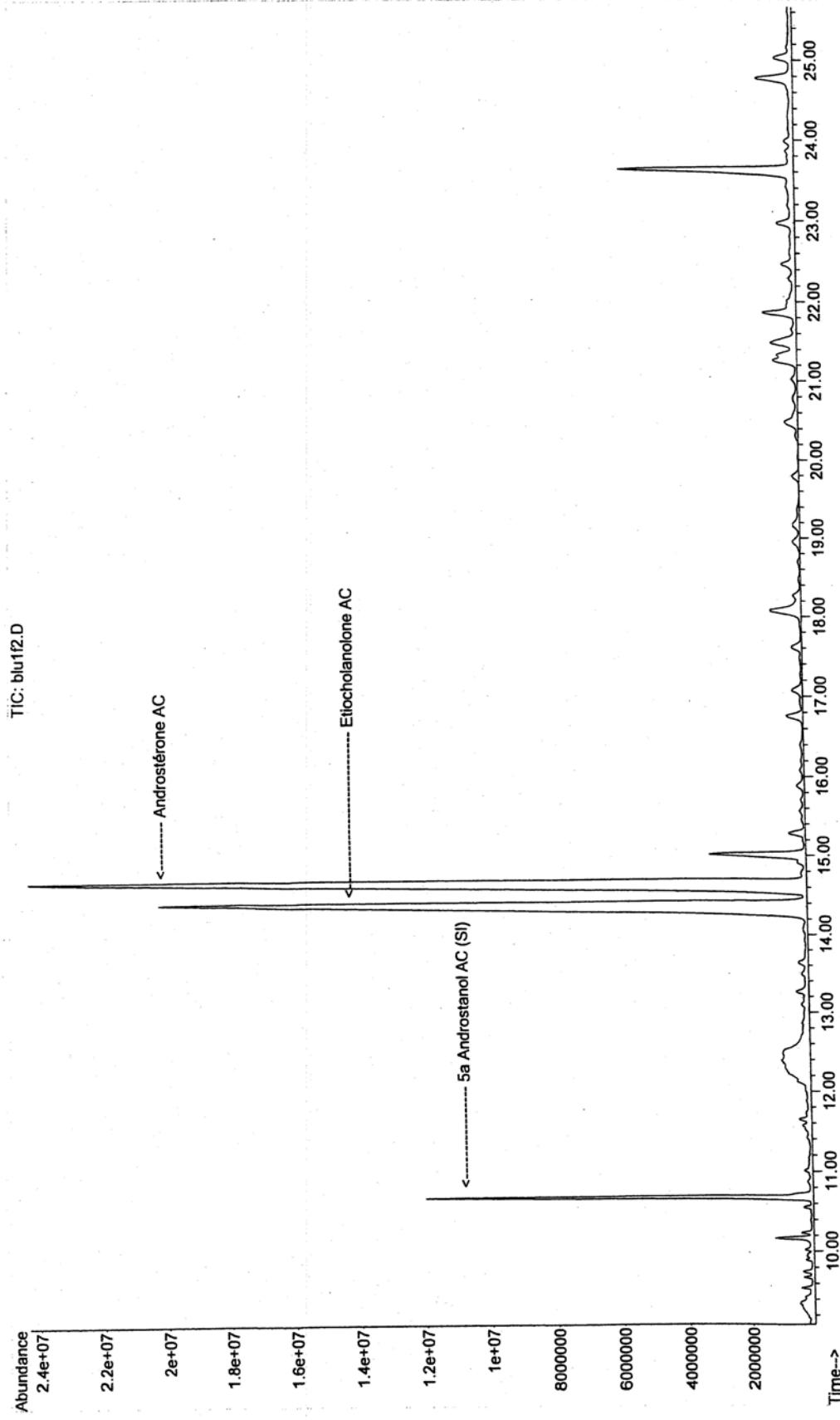
Time	Major	Ratio 2/1	Ratio 3/1
122.6	8.496E-8	1.1774E-2	4.2514E-3
182.6	8.501E-8	1.1773E-2	4.2514E-3
242.7	8.541E-8	1.1773E-2	4.2517E-3
2423.5	8.495E-8	1.1775E-2	4.2521E-3
2483.5	8.456E-8	1.1775E-2	4.2522E-3
2533.5	8.598E-8	1.1775E-2	4.2528E-3

Std Dev Of Fit 3.6976E-7 2.8218E-7

#### Analysis of Sample Peaks, with Background Subtraction

CO2	Time	Height	Area	2/1	3/1	dC13Pk	dC13Bkd	dO18Pk	dO18
	777.1	4.35E-9	2.3077E-8	1.1776E-2	4.1710E-3	-33.64	-129.52	-37.95	63
	870.2	2.90E-9	1.4257E-8	1.1809E-2	4.2083E-3	-31.08	-122.87	-29.33	42
	1490.1	2.72E-9	2.8456E-8	1.1879E-2	4.1846E-3	-24.75	-127.77	-34.88	58

File : D:\Msdd22\Aout06\0408\blu1f2.D  
Operator : 26 using AcqMethod MAN\_52.M  
Acquired : 4 Aug 2006 15:31  
Instrument : MSD22  
Sample Name: Blu 1 F2  
Misc Info : Blanc urinaire 1 Pool 4 Fraction 2 dans 400µL  
Vial Number: 6



USADA 0339

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# Optima GC 1.67-2 - Manual DP

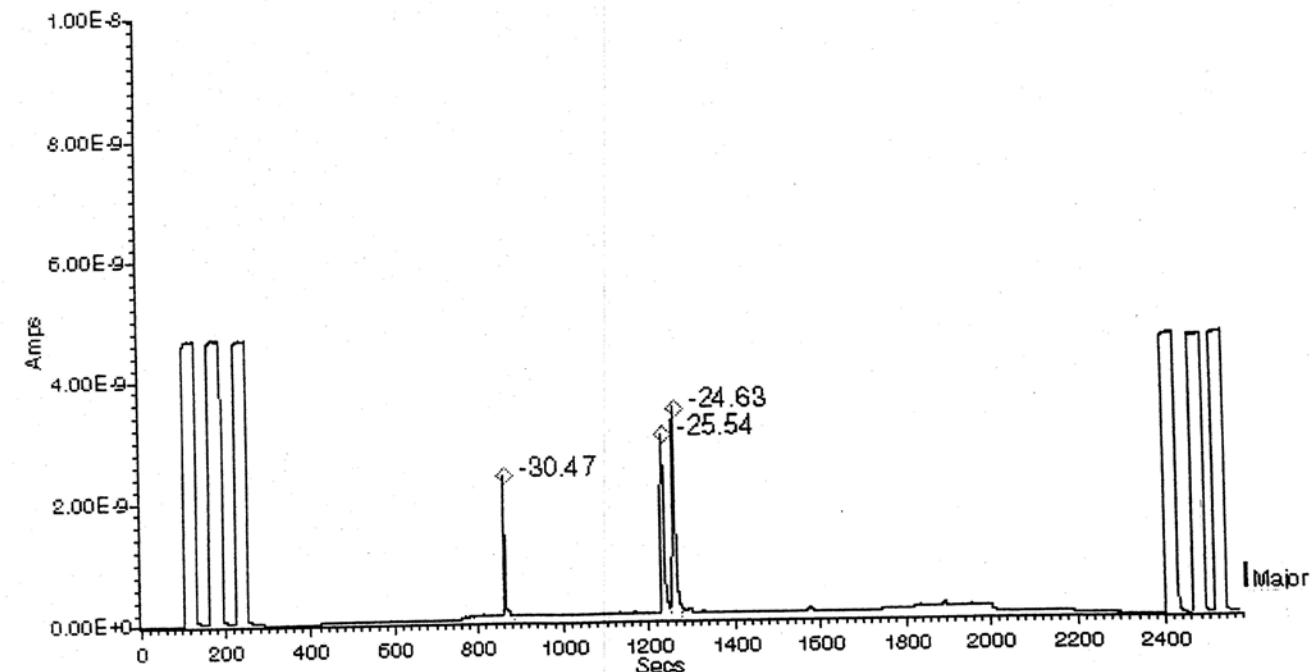
File Edit View Calculate Report Parameters Status Help

Data      Filename : DATA\_014      Folder : 040806  
Date : 04/08/06      Time : 20:02:53  
Comment : Blu 1 Pool 4 F2/1400uL inj 2uL

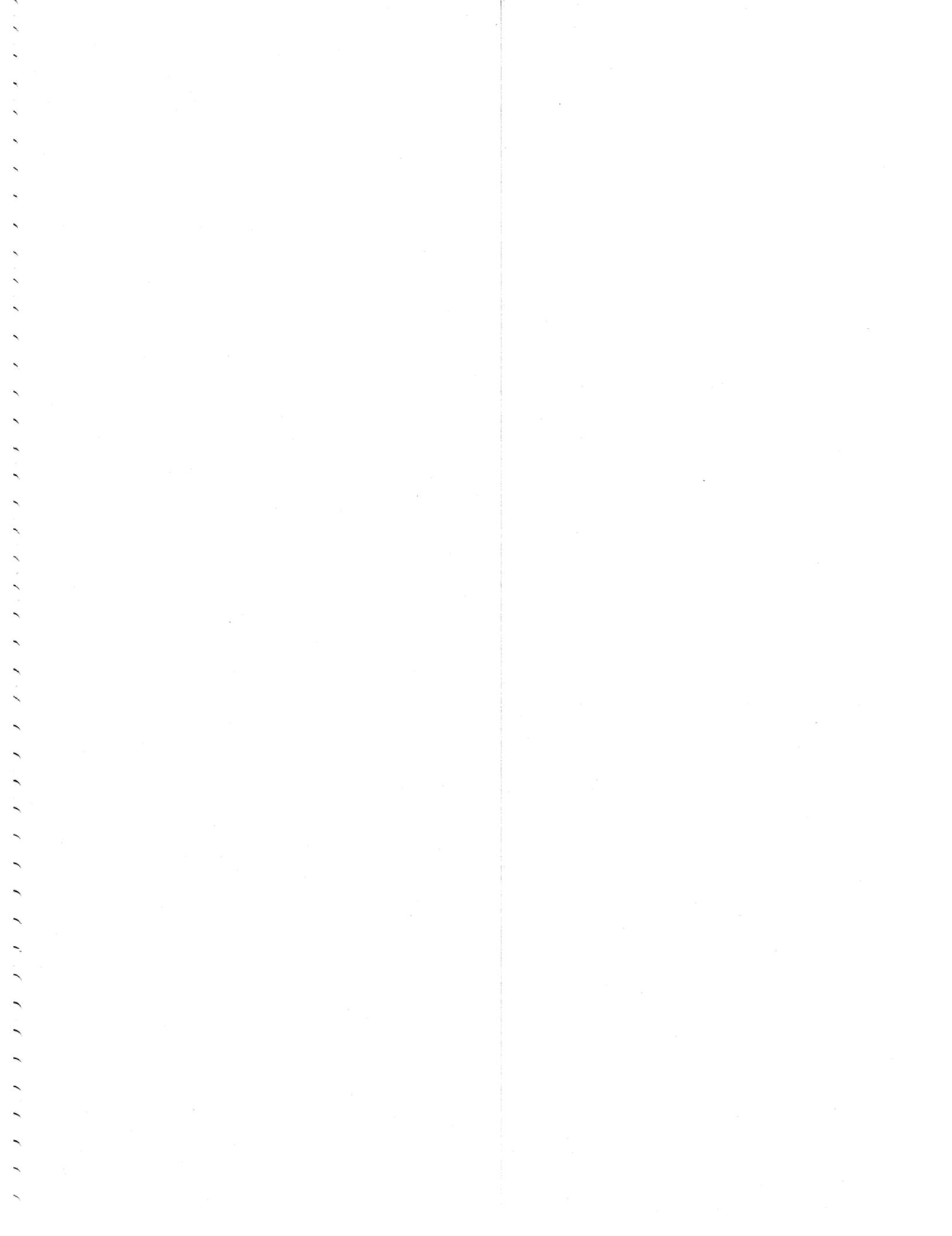
Parameters      Automatic DP Params

## ¤ Data Processing Main Graph

Graph Cursor Lines Window



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USADA 0340



### Data Processing Results

Data File Name : DATA\_014  
 Folder : 040806  
 Sample Name : Blu 1 Pool 4 F2/1400uL inj 2uL  
 Sample ID :  
 Sample Position : 7  
 Injection Size : 0.0000  
 Sample Type : Sam  
 Method : M-AN-41  
 Batch Name :  
 RunTime User : micromass  
 Acquisition Time : 20:02:53 Date : 04/08/06  
 Current Time : 08:18:20 Date : 05/08/06

#### Analysis of Reference Gas Data

Ref Delta 13 = -34.50 Ref Delta 18 = -19.30

Time	Major	Ratio 2/1	Ratio 3/1
122.6	8.496E-8	1.1776E-2	4.2531E-3
182.6	8.503E-8	1.1776E-2	4.2531E-3
242.6	8.494E-8	1.1776E-2	4.2528E-3
2423.5	8.442E-8	1.1774E-2	4.2519E-3
2483.5	8.385E-8	1.1774E-2	4.2515E-3
2533.5	8.462E-8	1.1773E-2	4.2518E-3

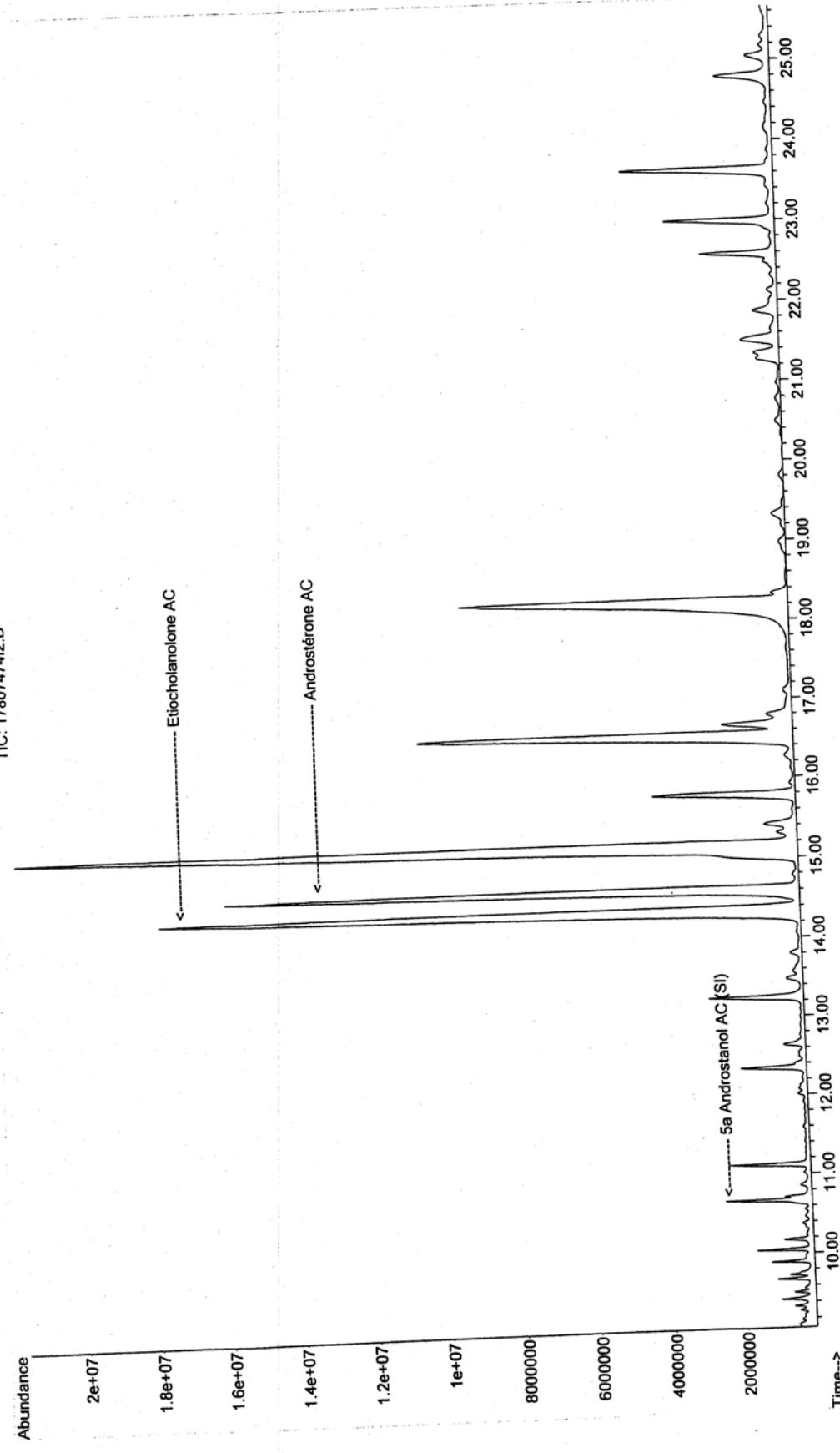
Std Dev Of Fit 3.6403E-7 1.7354E-7

#### Analysis of Sample Peaks, with Background Subtraction

CO<sub>2</sub>

Time	Height	Area	2/1	3/1	dc13Pk	dc13Bkd	d018Pk	d018
869.0	2.38E-9	1.2861E-8	1.1814E-2	4.1675E-3	-30.47	-71.51	-38.95	27
1241.0	3.05E-9	2.4953E-8	1.1870E-2	4.1678E-3	-25.54	-68.90	-38.86	27
267.5	3.48E-9	2.7395E-8	1.1880E-2	4.1669E-3	-24.63	-68.70	-39.06	27

File : D:\Msdd22\Aout06\0408\17807474£2.D  
Operator : 26 Aug 2006 16:03 using AcqMethod MAN\_52.M  
Acquired : 4 Aug 2006 16:03  
Instrument : MSD22  
Sample Name: 178/07 B 995474 F2  
Misc Info : 178/07 B 995474 Fraction 2 dans 400µL  
Vial Number: 7



USADA 0342

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DP Optima GC 1.67-2 - Manual DP

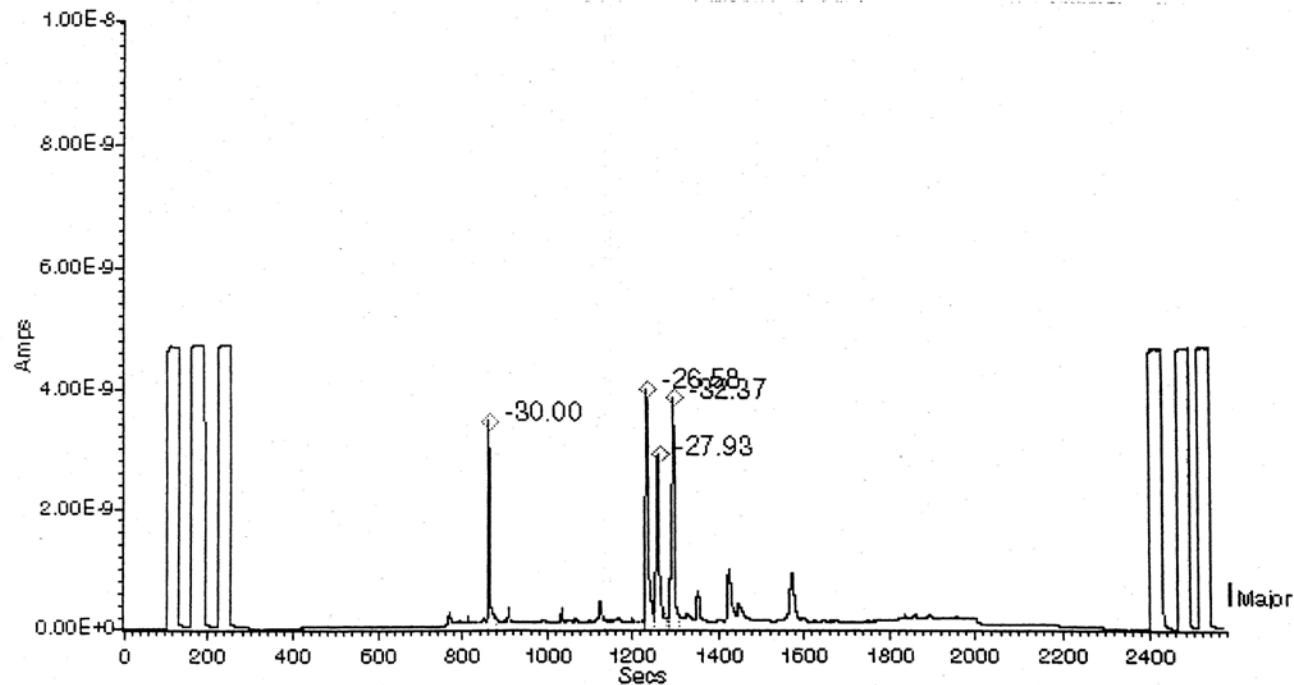
File Edit View Calculate Report Parameters Status Help

Data      Filename : DATA\_015      Folder : 040806  
Date : 04/08/06      Time : 20:47:38  
Comment : 178/07 995474 F2/850uL inj 2uL

Parameters      Automatic DP Params

✗ Data Processing Main Graph

Graph Cursor Lines Window



USADA 0343

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### Data Processing Results

Data File Name : DATA\_015  
 Folder : 040806  
 Sample Name : 178/07 995474 F2/850uL inj 2uL  
 Sample ID :  
 Sample Position : 8  
 Injection Size : 0.0000  
 Sample Type : Sam  
 Method : M-AN-41  
 Batch Name :  
 RunTime User : micromass  
 Acquisition Time : 20:47:38 Date : 04/08/06  
 Current Time : 08:03:23 Date : 05/08/06

Analysis of Reference Gas Data  
 Ref Delta 13 = -34.50 Ref Delta 18 = -19.30

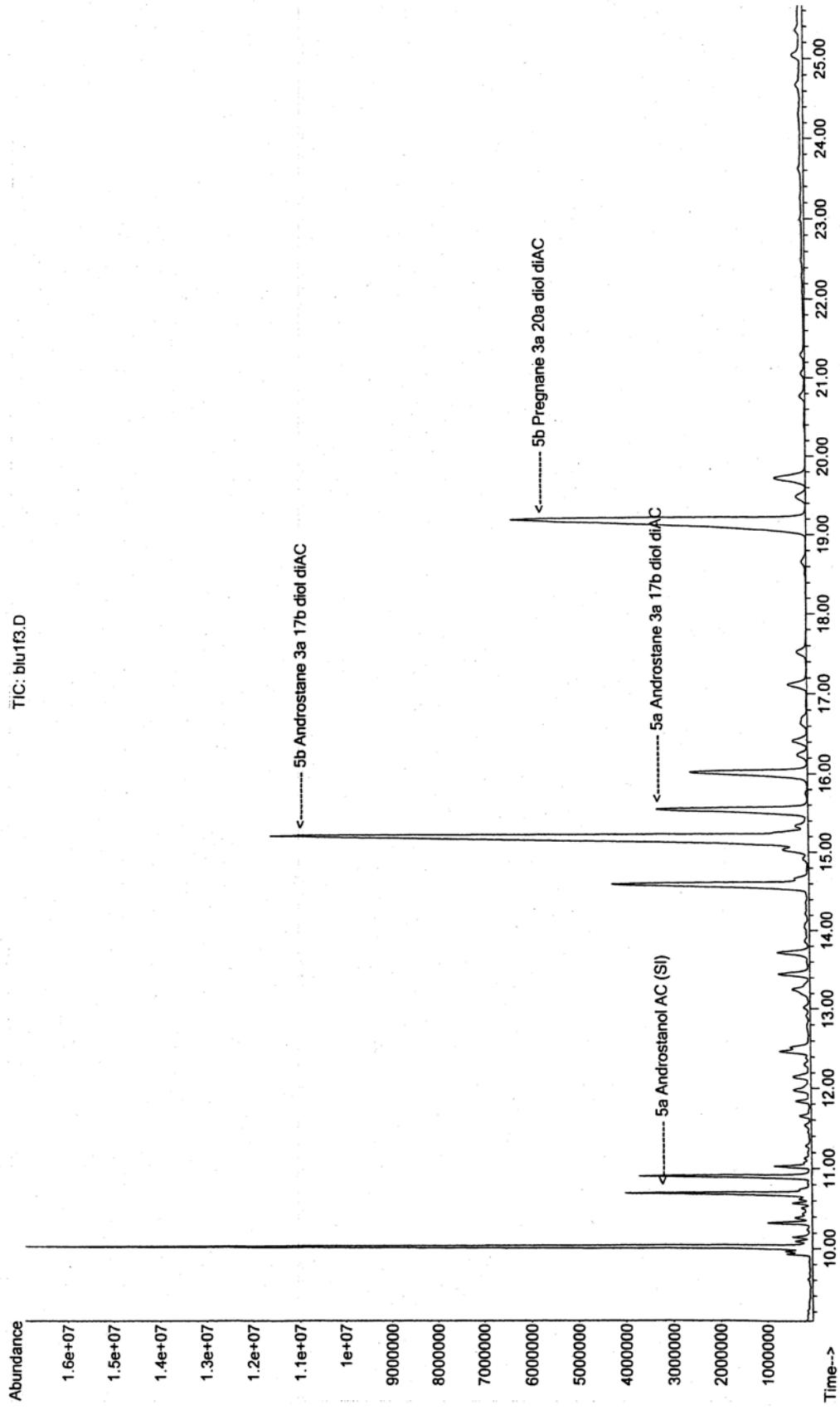
Time	Major	Ratio 2/1	Ratio 3/1
122.6	8.556E-8	1.1774E-2	4.2526E-3
182.5	8.604E-8	1.1775E-2	4.2533E-3
242.5	8.602E-8	1.1775E-2	4.2537E-3
2423.4	8.506E-8	1.1773E-2	4.2517E-3
2483.5	8.522E-8	1.1773E-2	4.2517E-3
2533.5	8.602E-8	1.1773E-2	4.2523E-3

Std Dev Of Fit 5.2841E-7 4.9662E-7

Analysis of Sample Peaks, with Background Subtraction

CO2	Time	Height	Area	2/1	3/1	dC13Pk	dC13Bkd	dO18Pk	dO18
	870.1	3.47E-9	1.6473E-8	1.1818E-2	4.1661E-3	-30.00	-65.04	-39.32	21
	1241.1	4.00E-9	3.2334E-8	1.1856E-2	4.1657E-3	-26.58	-61.51	-39.38	21
	1266.9	2.92E-9	2.1992E-8	1.1841E-2	4.1682E-3	-27.93	-60.71	-38.79	21
	1301.9	3.84E-9	3.1072E-8	1.1791E-2	4.1696E-3	-32.37	-59.44	-38.45	20

File : D:\Msd22\Aout06\0408\blu1f3.D  
 Operator : 26 Aug 2006 13:22 using AcqMethod MAN\_52.M  
 Acquired : 4 Aug 2006 13:22 using AcqMethod MAN\_52.M  
 Instrument : MSD22  
 Sample Name: Blu 1 F3  
 Misc Info : Blanc urinaire 1 Pool 4 Fraction 3 dans 100µL  
 Vial Number: 2



USADA 0345

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# Optima GC 1.67-2 - Manual DP

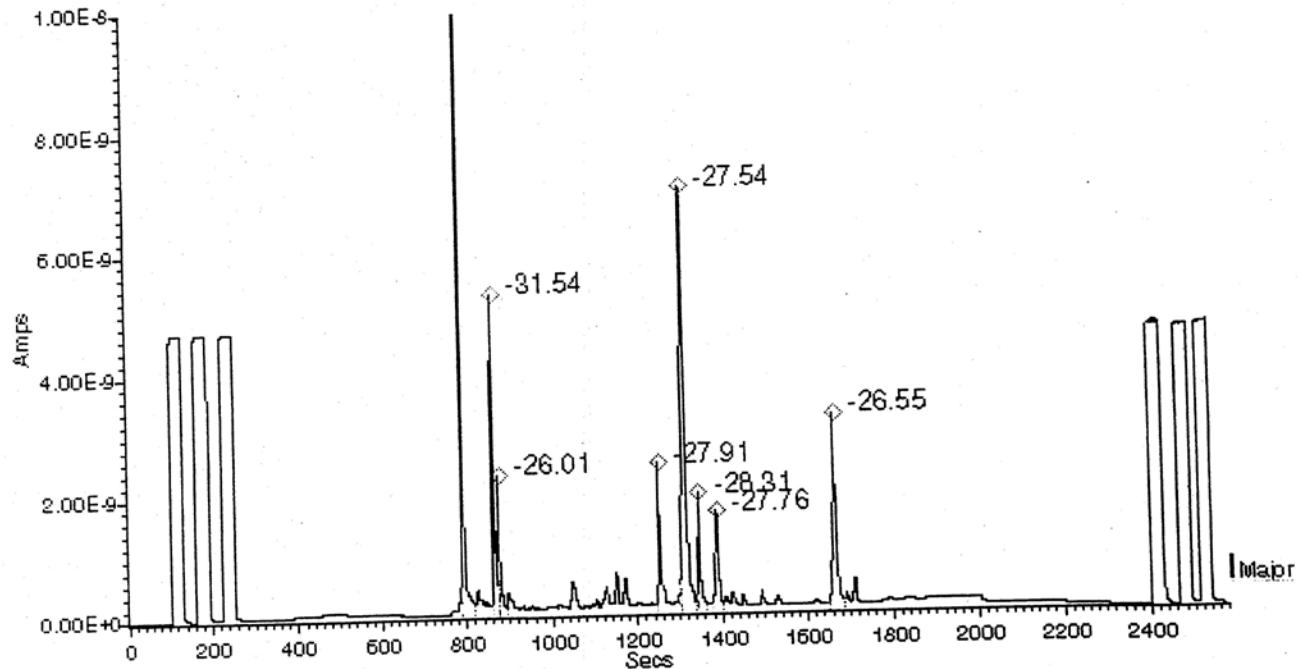
**File Edit View Calculate Report Parameters Status Help**

Data      Filename : DATA\_010      Folder : 040806  
Date : 04/08/06      Time : 17:03:53  
Comment : Blu 1 Pool 4 F3/45uL inj 2uL :

Parameters      Automatic DP Params

## ↓ Data Processing Main Graph

**Graph Cursor Lines Window**



### Data Processing Results

Data File Name : DATA\_010  
 Folder : 040806  
 Sample Name : Blu 1 Pool 4 F3/45uL inj 2uL  
 Sample ID :  
 Sample Position : 3  
 Injection Size : 0.0000  
 Sample Type : Sam  
 Method : M-AN-41  
 Batch Name :  
 RunTime User : micromass  
 Acquisition Time : 17:03:53 Date : 04/08/06  
 Current Time : 07:47:30 Date : 05/08/06

### Analysis of Reference Gas Data

Ref Delta 13 = -34.50 Ref Delta 18 = -19.30

Time	Major	Ratio 2/1	Ratio 3/1
122.6	8.545E-8	1.1774E-2	4.2514E-3
182.6	8.537E-8	1.1773E-2	4.2513E-3
242.7	8.497E-8	1.1773E-2	4.2507E-3
2423.5	8.468E-8	1.1772E-2	4.2505E-3
2483.5	8.400E-8	1.1772E-2	4.2507E-3
2533.5	8.435E-8	1.1772E-2	4.2508E-3

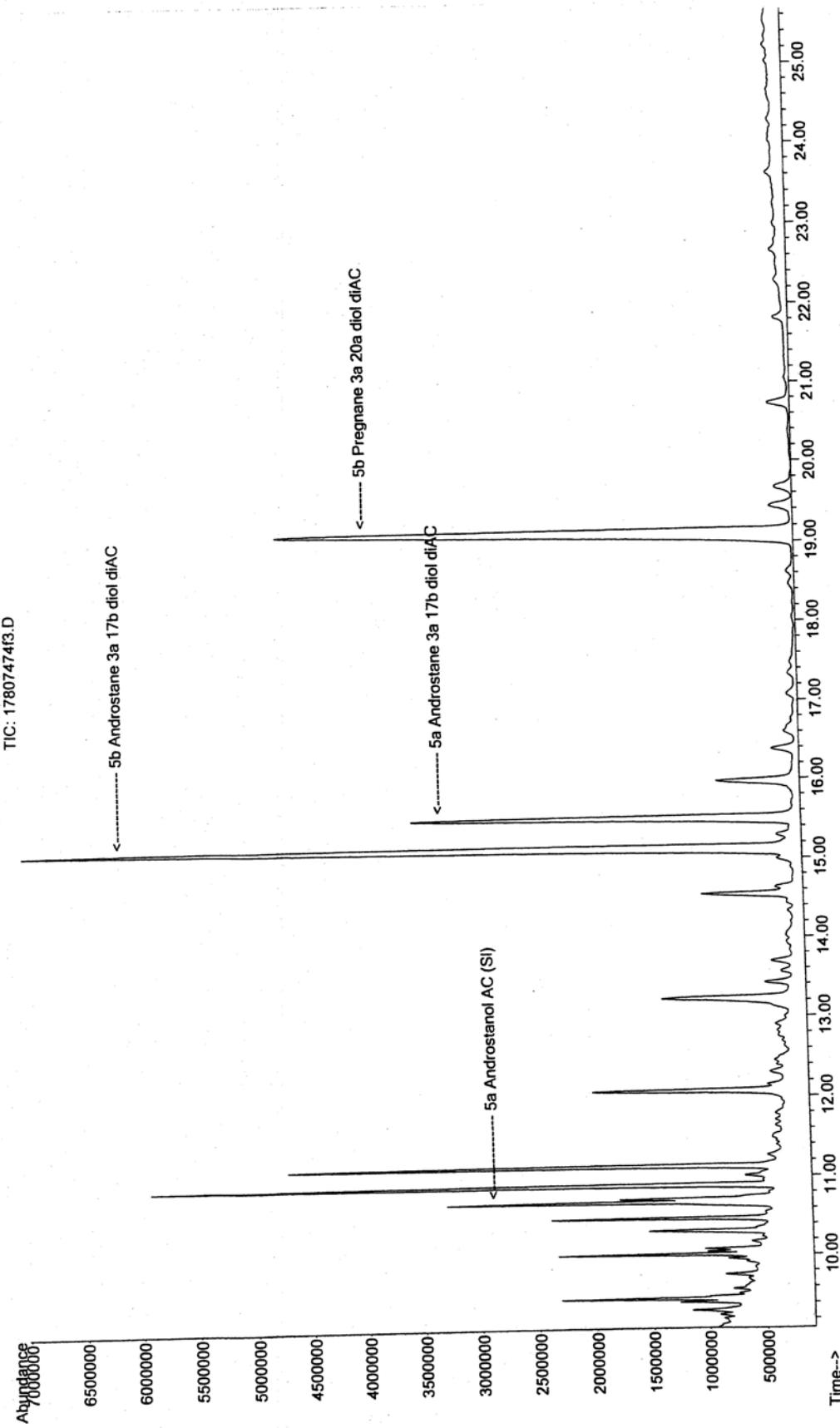
Std Dev Of Fit 3.7547E-7 2.7523E-7

### Analysis of Sample Peaks, with Background Subtraction

#### CO2

Time	Height	Area	2/1	3/1	dC13Pk	dC13Bkd	dO18Pk	dO18
799.0	1.36E-8	5.8132E-8	1.1877E-2	4.1762E-3	-24.77	-67.24	-36.59	17
872.4	5.30E-9	2.2912E-8	1.1801E-2	4.1836E-3	-31.54	-66.95	-34.88	17
881.1	2.34E-9	1.2956E-8	1.1867E-2	4.2171E-3	-26.01	-66.81	-27.15	17
1260.3	2.49E-9	2.2592E-8	1.1843E-2	4.1987E-3	-27.91	-65.40	-31.37	19
1323.0	7.04E-9	6.5008E-8	1.1845E-2	4.1705E-3	-27.54	-65.35	-37.87	20
1353.8	1.98E-9	1.6534E-8	1.1838E-2	4.1904E-3	-28.31	-65.37	-33.27	20
1394.3	1.68E-9	1.5157E-8	1.1844E-2	4.1913E-3	-27.76	-65.37	-33.08	20
1674.1	3.26E-9	3.5570E-8	1.1856E-2	4.1632E-3	-26.55	-65.86	-39.55	22

File : D:\Msd22\Aout06\0408\17807474f3.D  
Operator : 26  
Acquired : 4 Aug 2006 13:54 using AcqMethod MAN\_52.M  
Instrument : MSD22  
Sample Name: 178/07 B995474 F3  
Misc Info : 178/07 B 995474 Fraction 3 dans 100µL  
Vial Number: 3



USADA 0348

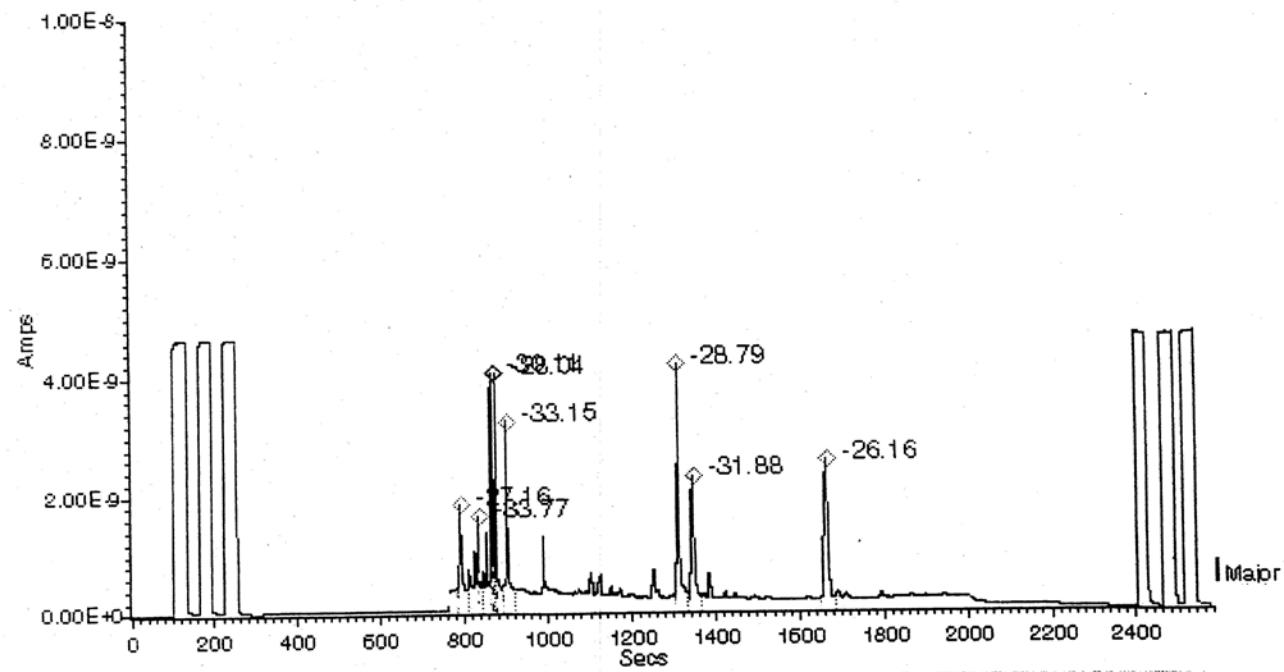
# Optima GC 1.67-2 - Manual DP

File Edit View Calculate Report Parameters Status Help

Data                   Filename : DATA\_011                   Folder : 040806  
                         Date : 04/08/06                   Time : 17:48:39  
                         Comment : 178/07 995474 F3/45uL inj 2uL :  
Parameters           Automatic DP Params

## ↓ Data Processing Main Graph

Graph Cursor Lines Window



USADA 0349

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### Data Processing Results

Data File Name : DATA\_011  
 Folder : 040806  
 Sample Name : 178/07 995474 F3/45uL inj 2uL  
 Sample ID :  
 Sample Position : 4  
 Injection Size : 0.0000  
 Sample Type : Sam  
 Method : M-AN-41  
 Batch Name :  
 RunTime User : micromass  
 Acquisition Time : 17:48:39 Date : 04/08/06  
 Current Time : 08:54:31 Date : 05/08/06

Analysis of Reference Gas Data  
 Ref Delta 13 = -34.50 Ref Delta 18 = -19.30

Time	Major	Ratio 2/1	Ratio 3/1
122.7	8.465E-8	1.1772E-2	4.2501E-3
182.7	8.465E-8	1.1771E-2	4.2504E-3
242.7	8.459E-8	1.1771E-2	4.2502E-3
2423.5	8.450E-8	1.1772E-2	4.2501E-3
2483.6	8.436E-8	1.1772E-2	4.2501E-3
2533.5	8.541E-8	1.1772E-2	4.2506E-3

Std Dev Of Fit 3.1407E-7 2.2560E-7

Analysis of Sample Peaks, with Background Subtraction

CO2

Time	Height	Area	2/1	3/1	dC13Pk	dC13Bkd	dO18Pk	dO18
797.1	1.84E-9	1.7724E-8	1.1857E-2	4.2650E-3	-27.16	-59.49	-15.91	8
839.1	1.63E-9	9.1742E-9	1.1778E-2	4.2295E-3	-33.77	-59.43	-24.09	9
871.9	4.08E-9	1.7193E-8	1.1816E-2	4.1820E-3	-30.11	-59.39	-35.07	9
880.6	4.07E-9	2.2454E-8	1.1841E-2	4.1969E-3	-28.04	-59.16	-31.63	9
909.0	3.27E-9	2.5928E-8	1.1785E-2	4.2250E-3	-33.15	-58.98	-25.14	9
1318.2	4.22E-9	3.9586E-8	1.1830E-2	4.1764E-3	-28.79	-57.10	-36.38	12
1352.4	2.33E-9	2.1502E-8	1.1796E-2	4.1861E-3	-31.88	-56.94	-34.13	12
1671.2	2.57E-9	2.9485E-8	1.1859E-2	4.1584E-3	-26.16	-55.38	-40.52	14

LNDD

## ENREGISTREMENT

Codification : E-FCR-06

Version : E

Date : 24/11/05

Page : 1/2

## FICHE D'ANALYSE / RESULTATS GC/C/IRMS

Echantillon : 178/07 B995474

Instrument : GC/C/IRMS Isoprime 1

Répertoire: 040806

CO et paraphe: 26CF

Valeur isotopique du réactif de dérivation: -53

Fraction F1 (métabolites de la cortisone et du cortisol)

Nom du fichier	Blanc urinaire		Echantillon	
	SI	11 Kétoétio	SI	11 Kétoétio
tr (s)	data_012	data_012	data_013	data_013
trr	870	1490	870	1490
Intensité (nA)	-	1.713	-	1.712
$\delta^{13}\text{C}$ ‰ mesurée	2.0	2.9	2.9	2.7
$\delta^{13}\text{C}$ ‰ corrigée	-30.45	-24.56	-31.08	-24.75
	-	-21.57	-	-21.78

Fraction F2 (Kétos)

Nom du fichier	Blanc urinaire			Echantillon		
	SI	Etio	Andro	SI	Etio	Andro
tr (s)	data_014	data_014	data_014	data_015	data_015	data_015
trr	869	1241	1268	870	1241	1267
Intensité (nA)	-	1.428	1.459	-	1.426	1.456
$\delta^{13}\text{C}$ ‰ mesurée	2.4	3.1	3.5	3.5	4.0	2.9
$\delta^{13}\text{C}$ ‰ corrigée	-30.47	-25.54	-24.63	-30.00	-26.58	-27.93
	-	-22.65	-21.64	-	-23.80	-25.29

Fraction F3 (Diols)

Nom du fichier	Blanc urinaire			
	SI	5 $\beta$ Adiol	5 $\alpha$ Adiol	5 $\beta$ Pdiol
tr (s)	data_010	data_010	data_010	data_010
trr	872	1323	1354	1674
Intensité (nA)	-	1.517	1.552	1.919
$\delta^{13}\text{C}$ ‰ mesurée	5.3	7.0	2.0	3.3
$\delta^{13}\text{C}$ ‰ corrigée	-31.54	-27.54	-28.31	-26.55
	-	-22.18	-23.11	-21.51

Nom du fichier	Echantillon			
	SI	5 $\beta$ Adiol	5 $\alpha$ Adiol	5 $\beta$ Pdiol
tr (s)	data_011	data_011	data_011	data_011
trr	872	1318	1352	1671
Intensité (nA)	-	1.512	1.551	1.917
$\delta^{13}\text{C}$ ‰ mesurée	4.1	4.2	2.3	2.6
$\delta^{13}\text{C}$ ‰ corrigée	-30.11	-28.79	-31.88	-26.16
	-	-23.69	-27.43	-21.05

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LNDD	ENREGISTREMENT	Codification : E-FCR-06
		Version : E
		Date : 24/11/05
		Page : 2/2

**FICHE D'ANALYSE / RESULTATS GC/C/IRMS**

	valeur de référence d'une population témoin		Echantillon dans les normes	
	$\delta^{13}\text{C}$ ‰ haute	$\delta^{13}\text{C}$ ‰ basse	oui	non
11 Kétoétio	-17.58	-26.27	α	
Etio	-19.56	-26.10	α	
Andro	-18.43	-25.02		α
5β Adiol	-18.55	-26.97	α	
5α Adiol	-18.59	-27.40		α
5β Pdiol	-18.25	-25.55	α	

	Blu	Echantillon		
		$\Delta\%$	$\Delta\% + 0,8\%$	$\Delta\%$
Etio - 11 Kétoétio	<b>-1.08</b>	-1.22	<b>-2.02</b>	-2.82
Andro - 11 Kétoétio	<b>-0.08</b>	-2.71	<b>-3.51</b>	-4.31
5β Adiol - 5β Pdiol	<b>-0.67</b>	-1.85	<b>-2.65</b>	-3.45
5α Adiol - 5β Pdiol	<b>-1.60</b>	-5.59	<b>-6.39</b>	-7.19

Seuil de positivité de l'AMA:  $\delta^{13}\text{C}$ ‰(métabolite) -  $\delta^{13}\text{C}$ ‰(composé endogène de référence)  $> 3\%$   
 $\delta^{13}\text{C}$  du composé  $< -28\%$

Variation maximale admissible liée à la méthode:  $\pm 0,8\%$

### Conclusion

L'analyse par spectrométrie de masse de rapport isotopique indique une origine exogène des métabolites de la testostérone, cohérente avec une prise de testostérone ou de l'un de ses précurseurs.

L'origine exogène des métabolites de la testostérone a été objectivée sur la base d'un appauvrissement isotopique de  $3.51\%$  et  $-6.39\%$  respectivement pour les métabolites androstérone et  $5\alpha$  androstanediol.

*Partie à remplir par le responsable*

Paraphe du responsable:

Observations:

USADA 0352

Ecart(s) n° :

*Cet enregistrement est à mettre dans le dossier de confirmation*

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LNDD

ENREGISTREMENT

Codification : E-CC-10

Version : C

Date : 09/05/2006

1/2

VERIFICATION DES PERFORMANCES INSTRUMENTALES EN CONFIRMATION  
CG/C/IRMS

Numéro d'échantillon : ... 178107 ... B795474 .....

Numéro d'identification de l'appareil : .... ISOPRANE 1 .....

Instruction de confirmation : ..... I CONF. 71 .....

1. TuneSpécification : plateau du peack Centre  $\geq$  10 VTune conforme : oui  non 2. Stabilité de l'instrumentSpécification: écart mesuré entre valeur maximale et valeur minimale du ratio 2/1  $\leq$  0.5 %Stabilité conforme : oui  non 3. Précision de l'instrument

Code de la solution Mix Cal IRMS: ..... 003 .....

Valeurs obtenues (%) pour 3 injections:

	Décane	Undécane	Dodécane	Méthyldécanoate
Moyenne	-32.36	-27.86	-31.86	-31.37
Ecart-type	0.04	0.11	0.10	0.10

Spécification: écart-type d'au moins 3 alcanes  $\leq$  0.5 %Précision conforme : oui  non

LNDD

ENREGISTREMENT

Codification : E-CC-10

Version : C

Date : 09/05/2006

2/2

**VERIFICATION DES PERFORMANCES INSTRUMENTALES EN CONFIRMATION  
CG/C/IRMS**

**4. Calibration de l'instrument**

Code de la solution Mix Cal Acétate: ... ~~001~~ A .....

**Valeurs obtenues (%) :**

	5a Androstanol AC	Etiocholanolone AC	5b Androstanediol diAC	11 Kétoetiocholanolone AC
date .009	-30.40	-19.98	-33.71	-16.74
date -016	-30.25	-19.95	-33.63	-16.67

**Intervalle de valeurs acceptables:**

	5a Androstanol AC	Etiocholanolone AC	5b Androstanediol diAC	11 Kétoetiocholanolone AC
Valeurs théoriques	-30.46	-19.91	-33.81	-16.30
Valeurs théoriques + 0.5%	-29.96	-19.41	-33.31	-15.80
Valeurs théoriques - 0.5%	-30.96	-20.41	-34.31	-16.80

Résultats conformes :

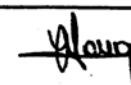
oui

non

**Résultats : CONFORME / NON CONFORME**  
Rayer la mention inutile

Observations:

**Validation**

Opérateur		Responsable	
Date	Code et Visa	Date	Code et Visa
4/8/16	280f	05/08/06	49 

*Cet enregistrement est à transmettre au responsable du secteur confirmation concerné  
puis à archiver vivant dans le dossier matériel de l'appareil concerné dans la section correspondante.*

USADA 0354

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## Optima GC 1.67-2

Inlet Mass Spec Scan Tests Analysis User Program Config Help

Current Mass : 45.00 Date : 04/06/06 Time : 10:21:22

Mass-44 = 4.6664E-9 A  
Mass-45 = 5.4958E-11 A  
Mass-46 = 2.0058E-11 A

FID = 0.11610 V

Srce status = 0

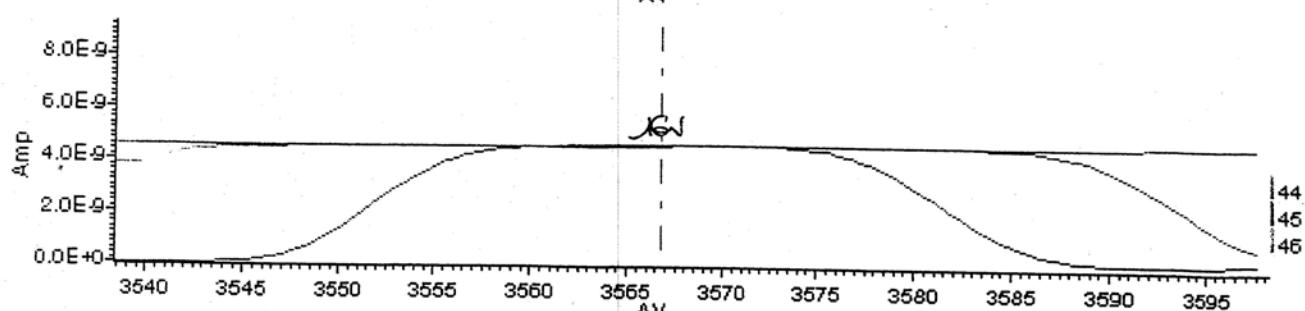
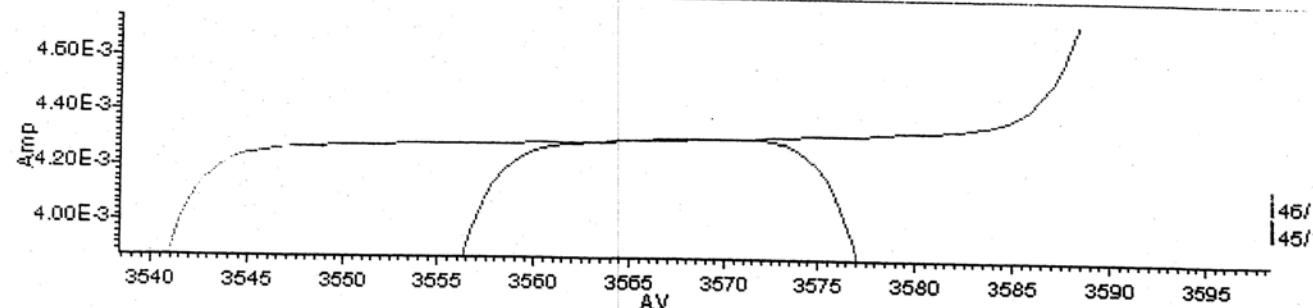
Penning = 2.8E-6 mBar

Pirani = 1.4E-2 mBar

Turbo speed= 1.0E+2 mBar

## Scan Display Window

Graph Cursor Lines Window Scan



### Data Processing Results

Data File Name : DATA\_005  
Folder : 040806  
Sample Name : Stabilite 5  
Sample ID :  
Sample Position : 1  
Injection Size : 0.0000  
Sample Type : Sam  
Method : CO2-STAB  
Batch Name : 040806  
RunTime User : micromass  
Acquisition Time : 11:08:45 Date : 04/08/06  
Current Time : 11:19:48 Date : 04/08/06

#### Analysis of Reference Gas Data

Ref Delta 13 = -34.50 Ref Delta 18 = -19.30

Time	Major	Ratio 2/1	Ratio 3/1
42.5	8.495E-8	1.1779E-2	4.2534E-3
102.5	8.499E-8	1.1779E-2	4.2535E-3
162.6	8.506E-8	1.1779E-2	4.2539E-3
222.6	8.502E-8	1.1779E-2	4.2538E-3
282.6	8.494E-8	1.1779E-2	4.2542E-3
342.6	8.489E-8	1.1779E-2	4.2543E-3
402.6	8.451E-8	1.1779E-2	4.2542E-3
462.7	8.487E-8	1.1779E-2	4.2543E-3
522.7	8.458E-8	1.1779E-2	4.2540E-3
582.7	8.439E-8	1.1779E-2	4.2538E-3

Std Dev Of Fit 1.7272E-7 2.7766E-7

#### Analysis of Sample Peaks, with Zero Subtraction

CO2

Time	Height	Area	2/1	3/1	dC13Pk	dO18Pk
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### Data Processing Results

Data File Name : DATA\_006  
Folder : 040806  
Sample Name : Mix Cal IRMS 003-1  
Sample ID :  
Sample Position : 1  
Injection Size : 0.0000  
Sample Type : Sam  
Method : M-AN-38  
Batch Name : 040806  
RunTime User : micromass  
Acquisition Time : 11:30:41 Date : 04/08/06  
Current Time : 11:46:25 Date : 04/08/06

### Analysis of Reference Gas Data

Ref Delta 13 = -34.50 Ref Delta 18 = -19.30

Time	Major	Ratio 2/1	Ratio 3/1
42.6	8.498E-8	1.1778E-2	4.2537E-3
102.6	8.503E-8	1.1778E-2	4.2534E-3
742.8	8.421E-8	1.1777E-2	4.2519E-3
802.9	8.412E-8	1.1776E-2	4.2519E-3

Std Dev Of Fit 1.2485E-7 1.0555E-7

### Analysis of Sample Peaks, with Zero Subtraction

CO2

Time	Height	Area	2/1	3/1	dC13Pk	dO18Pk
191.6	5.57E-9	1.4452E-8	1.1796E-2	4.1786E-3	-32.30	-36.54
259.1	4.36E-9	1.2956E-8	1.1848E-2	4.1803E-3	-27.78	-36.13
350.9	4.90E-9	1.4134E-8	1.1801E-2	4.1745E-3	-31.79	-37.39
538.2	5.18E-9	1.4106E-8	1.1805E-2	4.1624E-3	-31.30	-40.09

### Data Processing Results

Data File Name : DATA\_007  
Folder : 040806  
Sample Name : Mix Cal IRMS 003-2  
Sample ID :  
Sample Position : 1  
Injection Size : 0.0000  
Sample Type : Sam  
Method : M-AN-38  
Batch Name : 040806  
RunTime User : micromass  
Acquisition Time : 11:46:27 Date : 04/08/06  
Current Time : 12:06:32 Date : 04/08/06

### Analysis of Reference Gas Data

Ref Delta 13 = -34.50 Ref Delta 18 = -19.30

Time	Major	Ratio 2/1	Ratio 3/1
42.5	8.470E-8	1.1776E-2	4.2527E-3
102.6	8.526E-8	1.1777E-2	4.2529E-3
742.8	8.343E-8	1.1777E-2	4.2518E-3
802.8	8.391E-8	1.1776E-2	4.2516E-3

Std Dev Of Fit 4.2211E-7 1.2081E-7

### Analysis of Sample Peaks, with Zero Subtraction

CO2

Time	Height	Area	2/1	3/1	dC13Pk	dO18Pk
191.1	3.77E-9	8.8306E-9	1.1793E-2	4.1702E-3	-32.44	-38.33
257.4	2.88E-9	7.8902E-9	1.1844E-2	4.1722E-3	-27.99	-37.85
349.8	3.23E-9	8.7038E-9	1.1798E-2	4.1711E-3	-31.93	-38.05
536.7	3.50E-9	8.2134E-9	1.1803E-2	4.1643E-3	-31.44	-39.56

### Data Processing Results

Data File Name : DATA\_008  
Folder : 040806  
Sample Name : Mix Cal IRMS 003-3  
Sample ID :  
Sample Position : 1  
Injection Size : 0.0000  
Sample Type : Sam  
Method : M-AN-38  
Batch Name : 040806  
RunTime User : micromass  
Acquisition Time : 12:02:11 Date : 04/08/06  
Current Time : 12:21:06 Date : 04/08/06

Analysis of Reference Gas Data  
Ref Delta 13 = -34.50 Ref Delta 18 = -19.30

Time	Major	Ratio 2/1	Ratio 3/1
42.5	8.462E-8	1.1776E-2	4.2524E-3
102.6	8.517E-8	1.1776E-2	4.2526E-3
742.8	8.365E-8	1.1777E-2	4.2519E-3
803.1	8.370E-8	1.1776E-2	4.2520E-3

Std Dev Of Fit 4.2009E-7 1.8134E-7

Analysis of Sample Peaks, with Zero Subtraction

CO2

Time	Height	Area	2/1	3/1	dC13Pk	dO18Pk
191.1	5.45E-9	1.2876E-8	1.1793E-2	4.1690E-3	-32.33	-38.56
257.7	4.25E-9	1.1751E-8	1.1845E-2	4.1710E-3	-27.81	-38.09
349.8	4.83E-9	1.3084E-8	1.1799E-2	4.1708E-3	-31.80	-38.12
536.8	5.46E-9	1.2814E-8	1.1806E-2	4.1655E-3	-31.22	-39.31

### Data Processing Results

Data File Name : DATA\_009  
Folder : 040806  
Sample Name : Mix Cal Acetate 001A-100ng inj  
Sample ID :  
Sample Position : 2  
Injection Size : 0.0000  
Sample Type : Sam  
Method : M-AN-41  
Batch Name :  
RunTime User : micromass  
Acquisition Time : 12:24:14 Date : 04/08/06  
Current Time : 13:45:11 Date : 04/08/06

### Analysis of Reference Gas Data

Ref Delta 13 = -34.50 Ref Delta 18 = -19.30

Time	Major	Ratio 2/1	Ratio 3/1
122.5	8.507E-8	1.1776E-2	4.2528E-3
182.6	8.550E-8	1.1776E-2	4.2528E-3
242.6	8.493E-8	1.1776E-2	4.2530E-3
2423.4	8.422E-8	1.1775E-2	4.2523E-3
2483.5	8.354E-8	1.1775E-2	4.2518E-3
2533.5	8.443E-8	1.1775E-2	4.2521E-3

Std Dev Of Fit 9.2732E-8 1.7392E-7

### Analysis of Sample Peaks, with Background Subtraction

CO2

Time	Height	Area	2/1	3/1	dC13Pk	dC13Bkd	dO18Pk	dO18
870.6	4.30E-9	2.0644E-8	1.1815E-2	4.1628E-3	-30.40	-76.48	-40.04	32
1241.8	4.36E-9	3.5212E-8	1.1934E-2	4.1653E-3	-19.98	-74.28	-39.45	31
1316.7	3.35E-9	2.6894E-8	1.1777E-2	4.1662E-3	-33.71	-74.11	-39.21	31
1491.1	2.83E-9	3.1504E-8	1.1971E-2	4.1687E-3	-16.74	-74.00	-38.66	31

DP Optima GC 1.67-2 - Manual DP

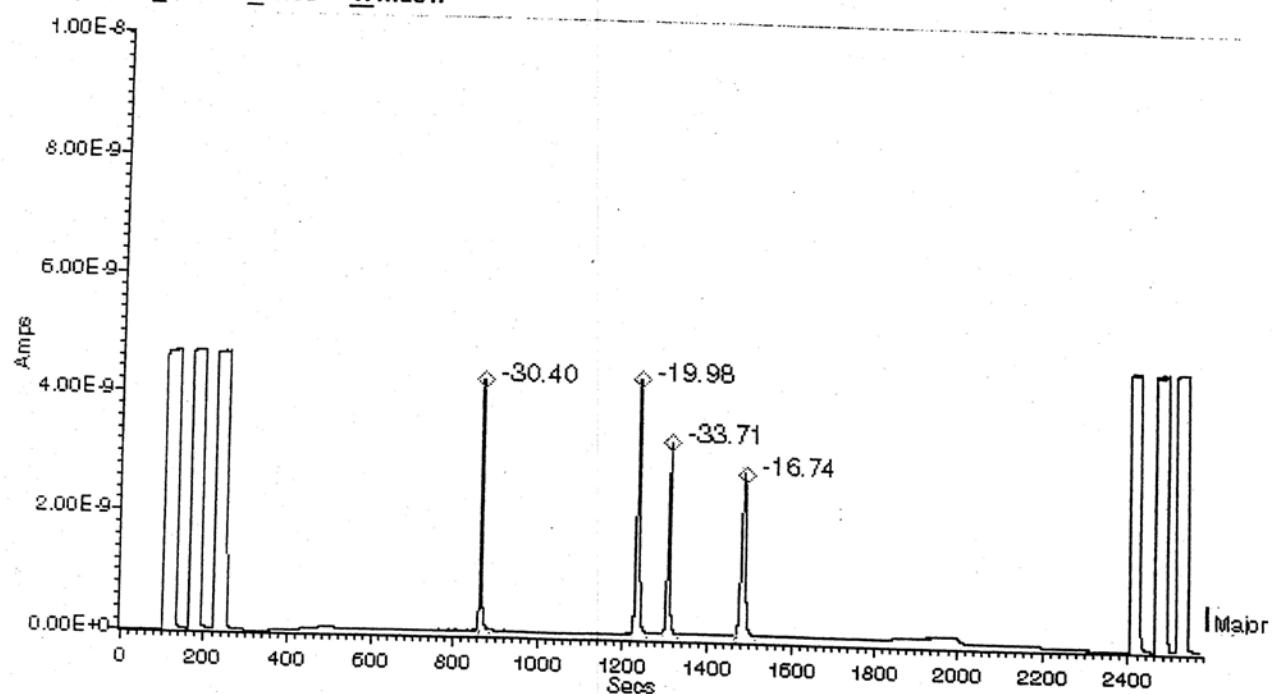
File Edit View Calculate Report Parameters Status Help

Data      Filename : DATA\_009      Folder : 040806  
Date : 04/08/06      Time : 12:24:14  
Comment : Mix Cal Acetate 001A-100ng inj

Parameters      Automatic DP Params

± Data Processing Main Graph

Graph Cursor Lines Window



USADA 0361

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### Data Processing Results

Data File Name : DATA\_016  
 Folder : 040806  
 Sample Name : Mix Cal Acetate 001A-100ng inj  
 Sample ID :  
 Sample Position : 9  
 Injection Size : 0.0000  
 Sample Type : Sam  
 Method : M-AN-41  
 Batch Name :  
 RunTime User : micromass  
 Acquisition Time : 21:32:21 Date : 04/08/06  
 Current Time : 07:33:19 Date : 05/08/06

Analysis of Reference Gas Data  
 Ref Delta 13 = -34.50 Ref Delta 18 = -19.30

Time	Major	Ratio 2/1	Ratio 3/1
122.5	8.534E-8	1.1775E-2	4.2534E-3
182.6	8.513E-8	1.1775E-2	4.2533E-3
242.6	8.502E-8	1.1774E-2	4.2532E-3
2423.4	8.433E-8	1.1774E-2	4.2522E-3
2483.4	8.404E-8	1.1774E-2	4.2518E-3
2533.5	8.484E-8	1.1773E-2	4.2521E-3

Std Dev Of Fit 4.6118E-7 1.1639E-7

Analysis of Sample Peaks, with Background Subtraction

CO<sub>2</sub>

Time	Height	Area	2/1	3/1	dC13Pk	dC13Bkd	dO18Pk	dO18
870.5	4.31E-9	1.9411E-8	1.1815E-2	4.1647E-3	-30.25	-79.02	-39.67	34
1241.6	4.22E-9	3.4868E-8	1.1933E-2	4.1679E-3	-19.95	-77.29	-38.91	33
1316.1	3.28E-9	2.7273E-8	1.1777E-2	4.1695E-3	-33.63	-77.27	-38.50	32
1490.4	2.97E-9	3.0767E-8	1.1970E-2	4.1690E-3	-16.68	-77.62	-38.62	32

DP Optima GC 1.67-2 - Manual DP

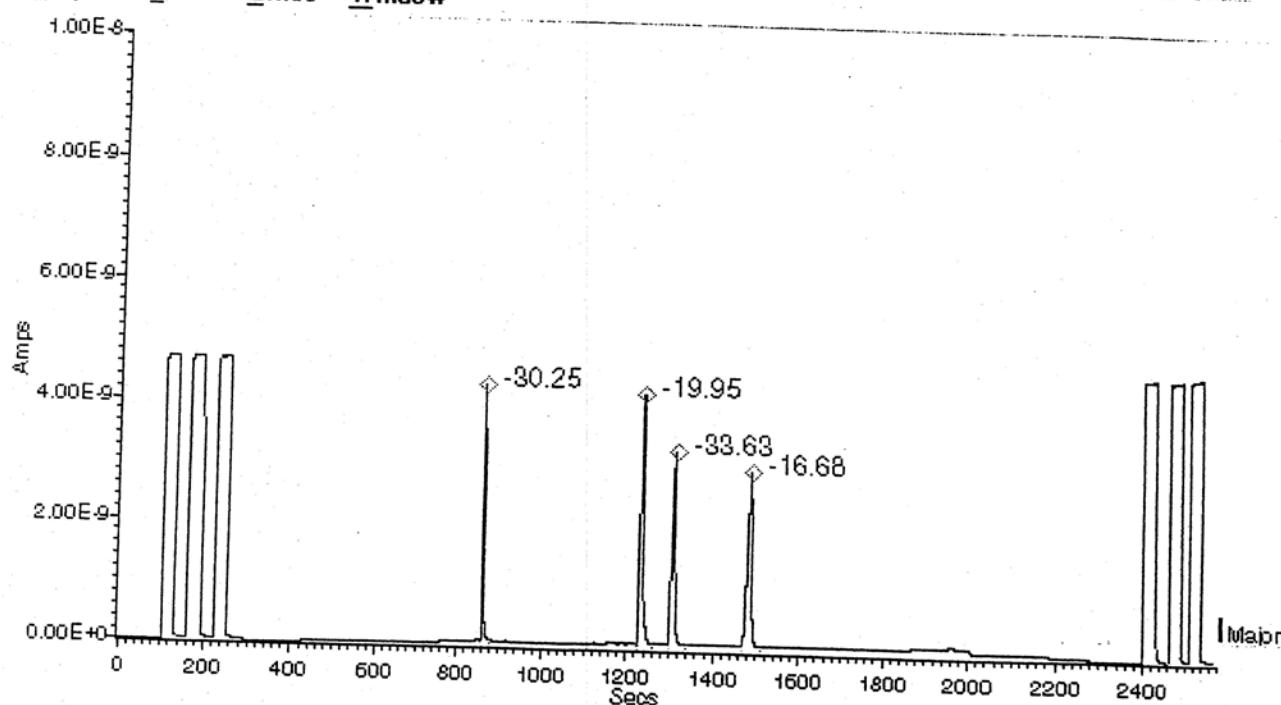
File Edit View Calculate Report Parameters Status Help

Data      Filename : DATA\_016      Folder : 040806  
Date : 04/08/06      Time : 21:32:21  
Comment : Mix Cal Acetate 001A-100ng inj

Parameters      Automatic DP Params

↳ Data Processing Main Graph

Graph Cursor Lines Window



USADA 0363

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RECEIVED  
Certificate of Analysis

USADA 0364

Châtenay-Malabry, le 05 août 2006

## RAPPORT DE CONTRE ANALYSE

*Demandes de contre-analyse de l'UCI et de l'USADA du 31 juillet 2006 suite au rapport d'analyse n°178/07-1*

### Prélèvements du Dr. BORDABERRY

Organisme : Cyclisme (UCI)  
Épreuve et lieu : TDF 2006 : 17<sup>ème</sup> étape à MORZINE  
Date : 20/07/2006

### Réception de(s) l'échantillon(s) d'urine :

Date : 20/07/2006  
Type de matériel : Berlinger  
Nombre d'échantillon(s) : 1 ( sur 3 échantillons reçus)  
Référence de(s) l'échantillon(s) : 178/07\_995474 B

*Résultats (Cf référentiels en vigueur : AMA / Réglementation nationale – contrôle en Compétition)*

Date de début des analyses : 03/08/2006

Méthodes utilisées : Chromatographie gazeuse couplée à la spectrométrie de masse GC/MS (EC24D) et  
Spectrométrie de masse de rapport isotopique GC/C/IRMS (EC31)

Conclusions : ( $pH = 5.2$        $d = 1.025 \pm 0.002$ )

T/E estimé à 11.0 (variation maximale admissible = 30%)

Concentration de Testostérone estimée après correction par la densité à 45.7 ng/mL  
(Variation maximale admissible = 20 %)

Concentration d'Epitestostérone estimée après correction par la densité à 4.2 ng/mL  
(Variation maximale admissible = 30 %)

Rapport supérieur au seuil de 4

\* Hors portée de l'accréditation COFRAC.

Le laboratoire n'est pas responsable du prélèvement des échantillons. La reproduction de ce rapport d'analyse n'est autorisée que sous sa forme intégrale. Il est confidentiel et comporte 2 page(s).

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## RAPPORT DE CONTRE ANALYSE (SUITE)

### Conclusions (Suite) :

L'analyse complémentaire par spectrométrie de masse de rapport isotopique indique une origine exogène des métabolites de la Testostérone, cohérente avec une prise de Testostérone ou de l'un de ses précurseurs.

L'origine exogène des métabolites de la Testostérone a été objectivée sur la base d'un appauvrissement isotopique de 6.4 ‰ et 3.5 ‰, respectivement pour les métabolites 5α-Androstanediol et Androstérone.

### Résultat exprimé par rapport au seuil de positivité de l'AMA :

- Appauvrissement isotopique > à 3 ‰ (*variation maximale admissible appliquée au laboratoire = 0.8‰*)

J. de CEAURRIZ  
Directeur

### Destinataires :

- Union Cycliste Internationale – C. VARIN (CH 1860 AIGLE - SUISSE)
- Président du Conseil de Prévention et de Lutte contre le Dopage (39 rue St Dominique - 75700 PARIS)

### Pour information :

- J. SOUBLIERE : WADA (fax n°00.1.514.904.18.00)
- Dr. GENSON - Chargé d'instruction à la Fédération Française de Cyclisme (4 rue du Poète - 33700 MERIGNAC)

\* Hors portée de l'accréditation COFRAC  
Le laboratoire n'est pas responsable du prélèvement des échantillons. La reproduction de ce rapport d'analyse n'est autorisée que sous sa forme intégrale. Il est confidentiel et comporte 2 page(s).

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ALUMINUM

USADA 0367

B-sample analysis 995474

Fifth of August 2006

Chatenay-Malabry

Statement no. 1

As an expert Dr. Douwe de Boer has been witnessing in the period between August 3 and August 5, 2006, the B-sample analysis in the LNDD, the WADA- accredited anti-doping laboratory in Chatenay-Malabry.

Statement no. 2

The impression of the expert regarding the analytical performance of the B-sample analysis was that the LNDD worked in a transparent and professional way and according to transparent and professional procedures.

Statement no. 3

In respect to the semi-quantitation of the ratio between testosterone and epitestosterone (T/E ratio) as well as of the concentration of testosterone and epitestosterone it must be stated the following:

- A) A ratio was established between two peaks in the chromatogram.
- B) The identity of the compound(s) belonging to the peaks has not been established according to the minimal WADA requirements.

Therefore, any official conclusion regarding to the T/E ratio as well as of the concentration of testosterone and epitestosterone is and will be premature. As such any official conclusion in relation to the above mentioned parameters of the respective sample is non-conclusive.

Statement no. 4

In respect to the GC/C/IRMS analysis it must be stated the following:

- A) During the B-sample analysis it was not possible to see documentation and data regarding the uncertainty of the GC/C/IRMS analysis, which was reported to be 0.8%.
- B) During the B-sample analysis it was not possible to see documentation and data regarding the historical data of blank urine pool no. 4.

Therefore, it was for the expert not possible to give an adequate evaluation of GC/C/IRMS analysis of the respective sample. The above mentioned issues have been implemented into a list of requests addressed to Prof. de Ceaurriz.

Dr Douwe de Boer



**List of the requests from Dr. Douwe de Boer**  
**Counter-analysis on "B" 995474**

➤ The GC/C/IRMS has been accredited by the WADA and the French National Accreditation body.

Would it be possible to see the documentation regarding this accreditation?  
If so, I would appreciate to see the documentation regarding the accreditation.

➤ In principle a WADA accredited laboratory is participating in proficiency programs.

Would it be possible to see data of the Châtenay-Malabry laboratory?  
If so, I would appreciate to see the data regarding the GC/C/IRMS analysis.

➤ The certificate of the analysis of the A-sample mentions an "uncertainty" of 0,8% for the GC/C/IRMS result.

Would it be possible to see documentation and data of how this value of "uncertainty" was established?

If so, I would appreciate to see documents and data regarding the establishment of the value of 0,8%.

➤ Historical data regarding the blank urine pool no.4, which has been used in the GC/C/IRMS procedure.

Would it be possible to see documentation and data regarding the history of blank urine pool no.4.

If so, I would appreciate to see the repeatability (intra-day variation) and the reproducibility (inter-day variation), meaning the average value, the standard deviation and the number of observations made.

Dr. Douwe de Boer



Expert

Pr. De Ceaarriz

  
Director